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(54) Preparation of olefin polymerisation catalyst component

(57) A process for producing a Gp IIa/transition metal olefin polymerisation catalyst component, in which a Gp IIa metal complex is reacted with a transition metal compound so as to produce an oil-in-oil emulsion, the disperse phase containing the preponderance of the Mg

being solidified by heating to provide a catalyst component of excellent morphology. Polymerisation of olefins using a catalyst containing such a component is also disclosed. The process may be employed in the production of Ziegler-Natta catalysts.

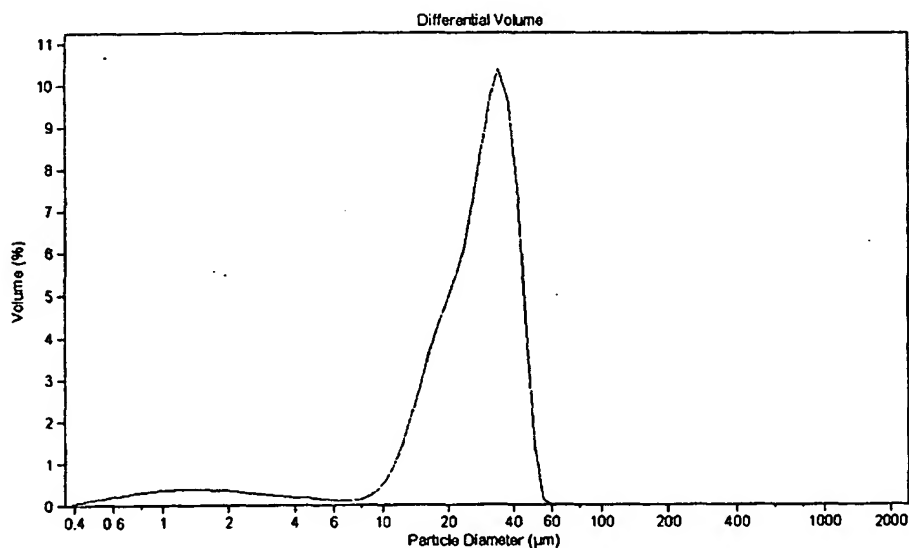


FIGURE 1

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Description

[0001] This invention relates to a process for the preparation of a particulate olefin polymerisation catalyst component, particularly one comprising a Gp IIA metal, a compound of a transition metal and an electron donor. The invention also relates to the use of such a catalyst component in the polymerisation of olefins.

Background of the invention

[0002] Processes for the preparation of such a catalyst component - as described, for instance, in WO 00/08073 and 00/08074 - usually include a step in which a magnesium-Gp IVB metal-electron donor component is recovered by precipitation from solution, typically by contacting the solution with a large amount of an aliphatic hydrocarbon. However, such precipitation leads to a tar-like reaction product of low catalytic activity, that needs to be washed several times in order to decrease the amount of inactive Gp IVB metal complex. Aromatic hydrocarbons have also been used for the precipitation, but they lead to a very finely divided precipitate which is difficult to deposit. Worse still, it is difficult to carry out such precipitation in a controlled and reproducible manner, leading to unsatisfactory product morphology. Moreover variable and low concentrations of catalyst constituents such as butyl chloride may result, as a consequence of pre-precipitation evaporative removal of aliphatic solvent.

Description of the invention

[0003] We have devised a new technique for recovering such a component from solution, which avoids the unsatisfactory precipitation previously practised and leads to an improved product morphology and consistent product composition.

[0004] According to the present invention a process for producing an olefin polymerisation catalyst component in the form of particles having a predetermined size range, comprises preparing a solution of a complex of a Gp IIA metal and an electron donor by reacting a compound of said metal with said electron donor or a precursor thereof in an organic liquid reaction medium; reacting said complex, in solution, with a compound of a transition metal to produce an emulsion the dispersed phase of which contains more than 50 mol% of the Gp IIA metal in said complex; maintaining the particles of said dispersed phase within the average size range 10 to 200 μm by agitation in the presence of an emulsion stabilizer and solidifying said particles; and recovering, washing and drying said particles to obtain said catalyst component.

[0005] The compound of a transition metal is preferably a compound of a Group IVB metal. The Group IVB metal is preferably titanium, and its compound to be reacted with the complex of a Gp IIA is preferably a halide. In a further embodiment of the invention a compound of a transition metal used in the process can also contain organic ligands typically used in the field known as a single site catalyst. In a still further embodiment of the invention a compound of a transition metal can also be selected from Group VB metals, Group VIB metals, Cu, Fe, Co, Ni and/or Pd. The complex of the Group IVA metal is preferably a magnesium complex. The invention will henceforth be described in relation to a preferred embodiment of the process, namely to a process for the preparation of a Ziegler-Natta type catalyst.

[0006] A preferred embodiment of the invention is a process for producing catalysts of the Ziegler-Natta type, in the form of particles having a predetermined size range, comprising: preparing a solution of magnesium complex by reacting an alkoxy magnesium compound and an electron donor or precursor thereof in a $\text{C}_6\text{-C}_{10}$ aromatic liquid reaction medium; reacting said magnesium complex with a compound of at least one IV valent Gp IVB metal at a temperature greater than 10°C and less than 60°C , to produce an emulsion of a denser, TiCl_4 /toluene-insoluble, oil dispersed phase having Gp IVB metal/Mg mol ratio 0.1 to 10 in an oil disperse phase having Gp IVB metal/Mg mol ratio 10 to 100; maintaining the particles of said dispersed phase within the size range 10 to 200 μm by agitation in the presence of an emulsion stabilizer while heating the emulsion to solidify said particles; and recovering, washing and drying said particles to obtain said catalyst component.

[0007] The said disperse and dispersed phases are thus distinguishable from one another by the fact that the denser oil, if contacted with a solution of titanium tetrachloride in toluene, will not dissolve in it. A suitable solution for establishing this criterion would be one having a Ti:toluene mol ratio of 0.1 to 0.3. They are also distinguishable by the fact that the great preponderance of the Mg provided (as complex) for the reaction with the Gp IVB metal compound is present in the dispersed phase, as revealed by comparison of the respective Gp IVB metal/Mg mol ratios.

[0008] In effect, therefore, virtually the entirety of the reaction product of the Mg complex with the Gp IVB metal - which is the precursor of the ultimate catalyst component - becomes the dispersed phase, and proceeds through the further processing steps to final dry particulate form. The disperse phase, still containing a useful quantity of Gp IVB metal, can be reprocessed for recovery of that metal.

[0009] The production of a two-phase, rather than single-phase (as in prior practice) reaction product is encouraged

by carrying out the Mg complex/Gp IVB metal compound reaction at low temperature, specifically above 10°C but below 60°C, preferably between above 20°C and below 50°C. Since the two phases will naturally tend to separate into a lower, denser phase and supernatant lighter phase, it is necessary to maintain the reaction product as an emulsion by agitation in the presence of an emulsion stabiliser.

5 [0010] The resulting particles of the dispersed phase of the emulsion are of a size, shape (spherical) and uniformity which render the ultimate catalyst component extremely effective in olefin polymerisation. This morphology is preserved during the heating to solidify the particles, and of course throughout the final washing and drying steps. It is, by contrast, difficult to the point of impossibility to achieve such morphology through precipitation, because of the fundamental uncontrollability of nucleation and growth, and the large number of variables which affect these events.

10 [0011] The electron donor is preferably an aromatic carboxylic acid ester, a particularly favoured ester being dioctyl phthalate. The donor may conveniently be formed in situ by reaction of an aromatic carboxylic acid chloride precursor with a C₂-C₁₆ alcohol and/or diol. The liquid reaction medium preferably comprises toluene.

[0012] The aforementioned emulsion stabiliser is typically a surfactant, of which the preferred class is that based on acrylic polymers.

15 [0013] It has been found that the best results are obtained when the Gp IVB metal/Mg mol ratio of the denser oil is 1 to 5, preferably 2 to 4, and that of the disperse phase oil is 55 to 65. Generally the ratio of the mol ratio Gp IVB metal/Mg in the disperse phase oil to that in the denser oil is at least 10.

[0014] Solidification of the dispersed phase particles by heating is suitably carried out at a temperature of 70-150°C, usually at 90-110°C. Preparation of the magnesium complex may be carried out over a wide range of temperatures, 20 to 80°C being preferred, 50 to 70°C most preferred.

20 [0015] The finally obtained catalyst component is desirably in the form of particles having an average size range of 10 to 200µm, preferably 20 to 50 µm.

[0016] The present invention further comprehends an olefin polymerisation catalyst comprising a catalyst component prepared as aforesaid, in association with an alkylaluminium cocatalyst, and the use of that polymerisation catalyst for the polymerisation of C₂ to C₁₀ α-olefins.

25 [0017] The reagents can be added to the aromatic reaction medium in any order. However it is preferred that in a first step the alkoxy magnesium compound is reacted with a carboxylic acid halide precursor of the electron donor to form an intermediate; and in a second step the obtained product is further reacted with the Gp IVB metal. The magnesium compound preferably contains from 1 to 20 cations per alkoxy group, and the carboxylic acid should contain at least 8 carbon atoms.

[0018] Reaction of the magnesium compound, carboxylic acid halide and polyhydric alcohol proceeds satisfactorily at temperatures in the range 20 to 80°C, preferably 50 to 70°C. The product of that reaction, the "Mg complex", is however reacted with the Gp IVB metal compound at a lower temperature, contrary to previous practice, to bring about the formation of a two-phase, oil-in-oil, product.

35 [0019] Use of the aromatic medium for preparation of the Mg complex contributes to consistent product morphology and higher bulk density. Catalyst bulk density and morphology correlate with product bulk density and morphology - the so-called "replication effect".

[0020] The technique adopted in the novel regimen of the invention is inherently more precise than that formerly employed, and thus further contributes to product consistency, as well as sharply reducing the volumes of solvent to be handled and thus improving process economics.

40 [0021] The aromatic liquid reaction medium used as solvent in the reaction is preferably selected from hydrocarbons such as substituted and unsubstituted benzenes, preferably from alkylated benzenes, more preferably from toluene and the xylenes, and is most preferably toluene. The molar ratio of said aromatic medium to magnesium is preferably less than 10, for instance from 4 to 10, preferably from 5 to 9.

45 [0022] The recovered particulate product is washed at least once, preferably at least twice, most preferably at least three times with a hydrocarbon, which preferably is selected from aromatic and aliphatic hydrocarbons, preferably with toluene, particularly with hot (e.g. 90°C) toluene. A further wash is advantageously performed with heptane, most preferably with hot (e.g. 90°C) heptane, and yet a further wash with pentane. A washing step typically includes several substeps. A favoured washing sequence is, for example, one wash with toluene at 90°C, two washes with heptane at 90°C and one or two washes with pentane at room temperature.

50 [0023] The washing can be optimised to give a catalyst with novel and desirable properties. Finally, the washed catalyst component is dried, as by evaporation or flushing with nitrogen.

[0024] It is preferable that the intermediates as well as the final product of the process be distinct compounds with an essentially stoichiometric composition. Often, they are complexes. A complex is, according to Römpps Chemie-Lexicon, 7. Edition, Franckh'sche Verlagshandlung, W. Keller & Co., Stuttgart, 1973, page 1831, "a derived name of compounds of higher order, which originate from the combination of molecules, - unlike compounds of first order, in the creation of which atoms participate".

55 [0025] The alkoxy magnesium compound group is preferably selected from the group consisting of magnesium di-

alkoxides, complexes of a magnesium dihalide and an alcohol, and complexes of a magnesium dihalide and a magnesium dialkoxide. It may be a reaction product of an alcohol and a magnesium compound selected from the group consisting of dialkyl magnesiums, alkyl magnesium alkoxides, alkyl magnesium halides and magnesium dihalides. It can further be selected from the group consisting of dialkyloxy magnesiums, diaryloxy magnesiums, alkyloxy magnesium halides, aryloxy magnesium halides, alkyl magnesium alkoxides, aryl magnesium alkoxides and alkyl magnesium aryloxides.

[0026] The magnesium dialkoxide may be the reaction product of a magnesium dihalide such as magnesium dichloride or a dialkyl magnesium of the formula R_2Mg , wherein each one of the two Rs is a similar or different C_1 - C_{20} alkyl, preferably a similar or different C_4 - C_{10} alkyl. Typical magnesium alkyls are ethylbutyl magnesium, dibutyl magnesium, dipropyl magnesium, propylbutyl magnesium, dipentyl magnesium, butylpentylmagnesium, butyloctyl magnesium and dioctyl magnesium. Most preferably, one R of the formula R_2Mg is a butyl group and the other R is an octyl group, i.e. the dialkyl magnesium compound is butyl octyl magnesium.

[0027] Typical alkyl-alkoxy magnesium compounds $RMgOR$, when used, are ethyl magnesium butoxide, butyl magnesium pentoxide, octyl magnesium butoxide and octyl magnesium octoxide.

[0028] Dialkyl magnesium, alkyl magnesium alkoxide or magnesium dihalide can react with a polyhydric alcohol $R'(OH)_m$ or a mixture thereof with a monohydric alcohol $R'OH$.

[0029] Typical C_2 to C_{16} polyhydric alcohols may be straight-chain or branched and include ethylene glycol, propylene glycol, trimethylene glycol, 1,2-butylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, 2,3-butylene glycol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, pinacol, diethylene glycol, triethylene glycol, and triols such as glycerol, trimethylol propane and pentarethritol. The polyhydric alcohol can be selected on the basis of the activity and morphology it gives the catalyst component.

[0030] The aromatic reaction medium may also contain a monohydric alcohol, which may be straight- or branched-chain. Typical C_1 - C_{20} monohydric alcohols are methanol, ethanol, n-propanol, iso-propanol, n-butanol, iso-butanol, sec.butanol, tert.butanol, n-amyl alcohol, iso-amyl alcohol, sec.amyl alcohol, tert.amyl alcohol, diethyl carbinol, akt. amyl alcohol, sec. isoamyl alcohol, tert.butyl carbinol. Typical C_6 - C_{10} monohydric alcohols are hexanol, 2-ethyl-1-butanol, 4-methyl-2-pentanol, 1-heptanol, 2-heptanol, 4-heptanol, 2,4-dimethyl-3-pentanol, 1-octanol, 2-octanol, 2-ethyl-1-hexanol, 1-nonanol, 5-nonanol, diisobutyl carbinol, 1-decanol and 2,7-dimethyl-2-octanol. Typical $>C_{10}$ monohydric alcohols are n-1-undecanol, n-1-dodecanol, n-1-tridecanol, n-1-tetra-decanol, n-1-pentadecanol, 1-hexadecanol, n-1-heptadecanol and n-1-octadecanol. The monohydric alcohols may be unsaturated, as long as they do not act as catalyst poisons.

[0031] Preferable monohydric alcohols are those of formula $R'OH$ in which R' is a C_2 - C_{16} alkyl group, most preferably a C_4 - C_{12} alkyl group, particularly 2-ethyl-1-hexanol.

[0032] Preferably, essentially all of the aromatic carboxylic acid ester is a reaction product of a carboxylic acid halide, preferably a dicarboxylic acid dihalide, more preferably an unsaturated α,β -dicarboxylic acid dihalide, most preferably phthalic acid dichloride, with the polyhydric alcohol.

[0033] The compound of a four-valent Gp IVB metal compound containing a halogen is preferably a titanium tetrahalide. Equivalent to titanium tetrahalide is the combination of an alkoxy titanium halide and a halogenation agent therefor, which are able to form a titanium tetrahalide *in situ*. The most preferred halide is the chloride, for zirconium and hafnium as well as for titanium.

[0034] The reaction conditions used in the claimed process may be varied according to the used reactants and agents.

[0035] As is known, the addition of at least one halogenated hydrocarbon during the process can lead to further improved catalytic activity. Reactive halogenated hydrocarbons preferably have the formula $R''X''_n$, wherein R'' is an n-valent C_1 - C_{20} hydrocarbyl group, particularly a C_1 - C_{10} paraffin, X'' is a halogen and n is an integer from 1 to 4.

[0036] Such chlorinated hydrocarbons include monochloromethane, dichloromethane, trichloromethane (chloroform), tetrachloromethane, monochloroethane, (1,1)-dichloroethane, (1,2)-dichloroethane, (1,1,1)-trichloroethane, (1,1,2)-trichloroethane, (1,1,1,2)-tetrachloroethane, (1,1,2,2)-tetrachloroethane, pentachloroethane, hexachloroethane, (1)-chloropropane, (2)-chloropropane, (1,2)-dichloropropane, (1,3)-dichloropropane, (1,2,3)-trichloropropane, (1)-chlorobutane, (2)-chlorobutane, isobutyl chloride, tert.butyl chloride, (1,4)-dichlorobutane, (1)-chloropentane, (1,5)-dichloropentane. The chlorinated hydrocarbons may also be unsaturated, provided that the unsaturation does not act as catalyst poison in the final catalyst component.

[0037] In the above formula, R'' is preferably a mono- or bivalent C_1 - C_{10} alkyl group, independently, X'' is preferably chlorine and, independently, n is preferably 1 or 2. Preferred compounds include butyl chloride (BuCl), dichloroalkanes such as (1,4)-dichlorobutane, and tertiary butyl chloride. Some preferred embodiments of the invention are described, by way of illustration, in the following Examples.

EXAMPLE 1

[0038] A magnesium complex solution was prepared by slowly adding over a 40 minute period, with stirring, 110 ml of a 20% solution in toluene of BOMAG-A (Tradename) $[\text{Mg}(\text{Bu})_{1.5}(\text{Oct})_{0.5}]$ to 38.9 ml of 2-ethylhexanol which had been cooled to 5°C in a 300 ml glass reactor. During the addition the reactor contents were maintained below 15°C. The temperature was then raised to 60°C and held at that level for 30 minutes with stirring, at which time reaction was complete. 6.4 ml phthaloyl chloride was then added over an 11 minute period. The reactor contents were stirred at 60°C for 20 minutes, 12.9 ml 1-chlorobutane was added, and stirring continued for another 15 minutes at 60°C. The resulting stable, yellowish Mg complex solution was cooled to room temperature.

[0039] 19.5 ml TiCl_4 , 5 ml heptane and 28.7 of the above-prepared Mg complex solution were reacted at 25°C in a 300 ml glass reactor. After 5 minutes, reaction was complete and a dark red emulsion had formed. The temperature was raised to 50°C, 2 ml of Viscoplex 1-254 (Tradename) (40-44% of acrylic polymer in base oil) was added, and the reactor contents were stirred for 30 minutes. The resulting stabilised emulsion was then heated to 90°C, with stirring, for 10 minutes to solidify the particles forming the dispersed phase. After settling and syphoning the solids (2.6 grams) underwent washing with:

1. 100 ml toluene at 90°C for 30 minutes;
2. 60 ml heptane, at 90°C for 20 minutes;
3. 60 ml heptane, at 35°C for 10 minutes;
4. 60 ml pentane, at 30°C for 5 minutes; and
5. 60 ml pentane, at 30°C for 5 minutes.

[0040] The solids were then dried at 60°C by nitrogen purge. The particles were established by microscopic examination to be perfectly spherical in shape. The Coulter PSD is shown in Figure 1.

EXAMPLE 2

[0041] Example 1 was repeated, in order to evaluate the consistency of the procedure. The quantity of solids product was 2.6g, the particles perfectly spherical. The Coulter PSD is shown in Figure 2.

EXAMPLE 3

[0042] Example 1 was repeated, the Viscoplex being replaced by 1.35g of poly(hexadecyl methacrylate) of average Mw 200,000. The product was again in the form of perfectly spherical particles.

[0043] The composition and morphology of the products of Examples 1 to 3 are summarised in the following table:

TABLE 1.

Example	Ti%	Mg%	DOP%*	Coulter** 10% μm	Coulter 50% μm	Coulter 90% μm
1	3.3	12.6	27.5	41.6	28	11.7
2	2.9	12.6	27.4	51.9	33.9	14.2
3	2.8	12.7	27.5	74.7	42.7	15.9

* Dioctyl phthalate (internal electron donor)

** Measured with Coulter LS 200 at room temperature with n-heptane as medium

EXAMPLES 4 to 6

[0044] The products of Examples 1 to 3 were evaluated as catalyst components in propylene polymerisation in the following manner.

[0045] 0.9 ml triethyl aluminium (TEA) (co-catalyst), 0.12 ml cyclohexyl methyl dimethoxy silane (CMMS) as an external donor and 30 ml n-pentane were mixed and allowed to react for 5 minutes. Half of the mixture was then added to a polymerisation reactor and the other half was mixed with 20 mg of the components prepared in Examples 1 and 2. After an additional 5 minutes the component TEA/donor/n-pentane mixture was added to the reactor. The Al/Ti mole ratio of the resulting polymerisation catalyst was 250 mol/mol and the Al/CMMS mole ratio was 10 mol/mol.

[0046] Propylene bulk polymerisation was carried out in a stirred 5 l tank reactor.

[0047] 70 mmol hydrogen and 1400 g propylene were introduced into the reactor and the temperature was raised

within 15 minutes to the polymerisation temperature of 70°C. The polymerisation time at 70°C was 60 minutes, after which the polymer formed was taken out from the reactor. Example 3 employed the catalyst containing component of Example 1, Example 4 that of Example 2, Example 6 that of Example 3.

[0048] The results of the polymerisation evaluations are summarised in the following Table.

TABLE 2

Example	Activity kgPP/gCat	MFR ¹ g/10m in	XS ² %	BD ³ g/ml	% particles <0.1 mm
4	24.1	5.5	1.7	0.45	0
5	24.4	4.1	1.4	0.44	0
6	21.2	7.0	2.5	0.44	0

¹ ISO 1133, 2.16 kg load at 230°C

² xylene-soluble fraction of product at 25°C

³ polymer-bulk density (ASTM D 1895)

[0049] The polymer particles were spherical, with a markedly narrow size distribution: more than 75% of the product was of 0.5-1.00 mm particle diameter.

Claims

1. A process for producing an olefin polymerisation catalyst component in the form of particles having a predetermined size range, comprising:

preparing a solution a complex of a Gp Ila metal and an electron donor by reacting a compound of said metal with said electron donor or a precursor thereof in an organic liquid reaction medium;
 reacting said complex, in solution, with at least one compound of a transition metal to produce an emulsion the dispersed phase of which contains more than 50 mol% of the Gp Ila metal in said complex;
 maintaining the particles of said dispersed phase within the average size range 10 to 200 µm by agitation in the presence of an emulsion stabilizer and solidifying said particles; and
 recovering, washing and drying said particles to obtain said catalyst component.

2. A process according to claim 1 wherein said transition metal is a Gp IVB metal.
3. A process according to claim 1 or claim 2 wherein said Gp Ila metal is magnesium.
4. A process according to any preceding claim wherein said medium comprises a C₆-C₁₀ aromatic hydrocarbon.
5. A process according to any preceding claim wherein said emulsion is composed of a dispersed phase which is a TiCl₄/toluene-insoluble oil having a Gp IVB metal/Mg mol ratio greater than 0.1 and less than 10 and a disperse phase which is an oil less dense than that of the dispersed phase and which has a Gp IVB metal/Mg mol ratio of 10 to 100.
6. A process according to claim 5 wherein the Gp IV metal/Mg mol ratio of said disperse phase is 20 to 80.
7. A process according to claim 5 wherein the Gp IV metal/Mg mol ratio of said disperse phase is 45 to 75.
8. A process according to any preceding claim wherein said complex and said transition metal compound are reacted at a temperature of 10 to 60°C.
9. A process according to any preceding claim wherein the solidification of said particles is effected by heating.
10. A process according to any preceding claim wherein said electron donor is an aromatic carboxylic acid ester.
11. A process according to any preceding claim wherein said electron donor is dioctyl phthalate.

12. A process according to any preceding claim wherein said electron donor is formed in situ by reaction of an aromatic carboxylic acid chloride precursor with a C₂-C₁₆ alkanol and/or diol.
13. A process according to any preceding claim wherein said liquid reaction medium comprises toluene.
14. A process according to any of claims 2 to 13 wherein said Gp IVB metal is titanium.
15. A process according to any of claims 2 to 14 wherein said compound of a Gp IVB metal is a halide.
16. A process according to any of claims 3 to 15 wherein said magnesium complex and Gp IVB metal compound are reacted at a temperature of greater than 20°C to less than 50°C.
17. A process according to any preceding claim wherein said emulsion stabilizer is a surfactant.
18. A process according to claim 17 wherein said surfactant comprises an acrylic polymer.
19. A process according to any of claims 5 to 18 wherein the Gp IVB metal/Mg mol ratio of said denser oil is 2 to 4 and that of the disperse phase oil is 55 to 65.
20. A process according to claim 19 wherein the ratio of the mol ratio Gp IVB metal/Mg in the disperse phase oil to that in said denser oil is at least 10.
21. A process according to any of claims 8 to 20 wherein the emulsion is heated to a temperature of 70-150°C to solidify said particles.
22. A process according to claim 21 wherein the temperature to which the emulsion is heated is 90-110°C.
23. A process according to any preceding claim wherein the preparation of the Gp IIa metal complex is carried out at a temperature of 20 to 80°C.
24. A process according to 23 wherein the Gp IIa metal is magnesium and the preparation of the magnesium complex is carried out at a temperature of 50 to 70°C.
25. A process according to claim 1 wherein said transition metal is a Gp VB metal and/or a Gp VIB metal.
26. A process according to claim 1 wherein said transition metal is Cu, Fe, Co, Ni and/or Pd.
27. A process according to any preceding claim wherein said obtained catalyst component is in the form of particles having an average size range of 10 to 200µm.
28. A process according to claim 27 wherein said particles have an average size range of 20 to 50 µm.
29. An olefin polymerisation catalyst comprising a catalyst component prepared according to any of claims 1 to 28 and an alkylaluminium cocatalyst.
30. Use of a catalyst in accordance with claim 29 for the polymerisation of C₂ to C₁₀ α-olefins.

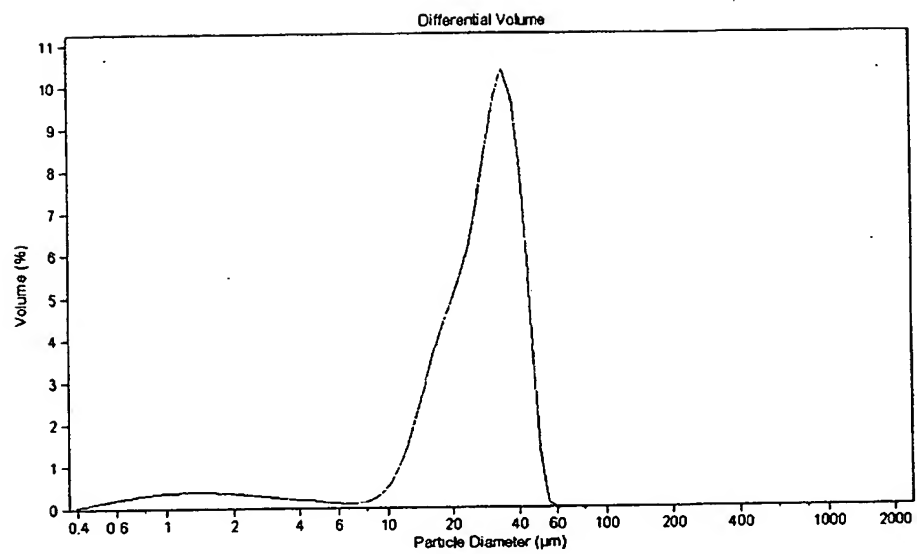


FIGURE 1

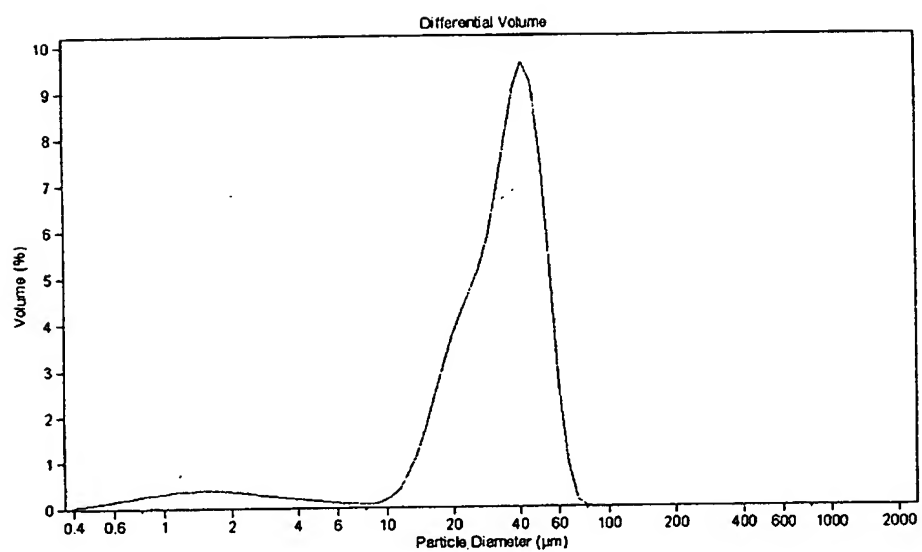


FIGURE 2



European Patent
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EUROPEAN SEARCH REPORT

Application Number
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Place of search THE HAGUE		Date of completion of the search 28 November 2001	Examiner Gamb, V
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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